UV absorption spectra of polyamide acids and their amine salts

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Abstract

We prepared a series of polyamide acids and polyamide acid amine salts PMDA-PDA, BPDA-PDA, BTDA-PDA, PMDA/DCHM, BPDA/DCHM, BTDA/DCHM and studied the UV absorption spectra of polyamide acids, their amine salts, as well as their model compounds, and try to discuss the factor which affect their absorption peaks and indensity.

Introduction

With superior thermal and mechanical properties and low dielectric constant, polyimides have been widely used in the electronics industry.[1] Being insoluble in most common solvents, polyimides are usually processed in the form of their precursors, polyamide acids, which are then thermally converted to the imide structure. However, most polyamide acids are soluble only in strongly polar solvents which need careful handling. In our previous study,[2] it was found that the amine salts of polyamide acids are soluble in water, and that their color is different from the original polyamide acids.

In this report, several polyamide acid amine salts were prepared and their UV absorption spectra were studied. Also, we will discuss the factors which affect their absorption with model compounds.

Experiments

A series of polyamide acids were prepared by the ordinary process, with pyromellitic dianhydride(PMDA), 3,4,3',4'-biphenyltetracarboxylic dianhydride(BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride(BTDA), as dianhydrides, and p-phenylene-diamine(PDA)and 4,4'-diaminodicyclohexylmethane as diamines. Polyamide acid amine salts(PASs) were prepared by mixing an equimolar ratio of polyamide acids and triethanolamine in dimethylacetamide(DMF). The UV absorption spectra of both PAAs

and PASs were measured with a Jasco V-570 UV/VIS spectrophotometer in dimethylformamide(DMF) and in water solution.

Results and discussion

In order to elucidate the relationship between molecular structure and absorption properties, we selected three kinds of aromatic tetracarboxylic dianhydride PMDA, BPDA, BTDA to react with PDA and DCHM to form polyamide acids and their amine salts in this research.

All the samples of these polyamide acid amine salts are soluble in water. According to IR spectra, we could say all the polyamide acids were converted to polyamide acid amine salts completely because of the disappearance of C=O absorption peak in 1710cm^{-1} in the absorption spectra of the amine salts.

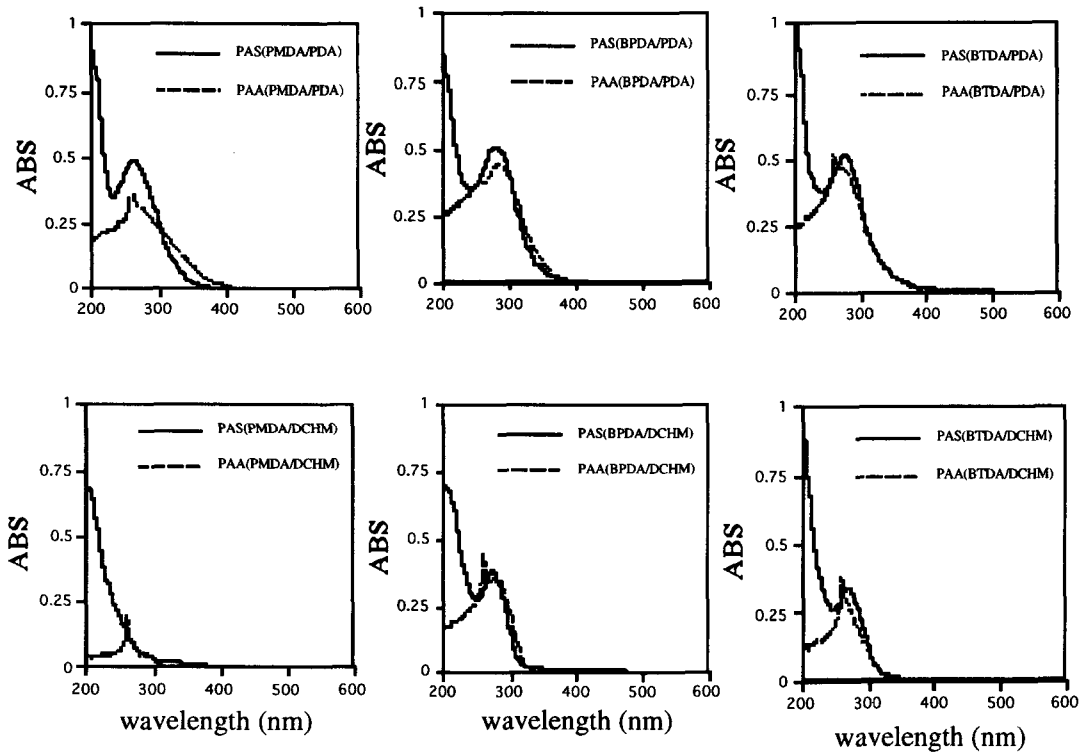

Fig.1. The UV spectra of PASs (1.60x10^{-5}M,H_2O), and PAAs (1.60x10^{-4}M, DMF, referenece, 1mm cell)

Fig.1.is the UV absorption spectra of 6 kinds of PAAs and PASs . As can be seen, the absorption of PASs is blue shifted than PAAs, as well as the increase in intensity.

Especially, the absorption tailing of PAS(PMDA/PDA) is cutted clearly compared to PAA(PMDA/PDA). Also, the absorption of the PASs with aromatic diamine are red shifted with the increase in intensity, compared to the PASs with alicyclic diamine, especially in the case of PMDA. Same tendency are found in the corresponding model compounds of the PASs and PAAs (Fig.2.), which the absorption tailings of all the MASs with aromatic diamine are cutted. PASs and MASs in water would form hydrogen bond with water, which will shorten the conjugation of the polymer chain, accordingly, the absorption of PASs and MASs in water are blue shifted.

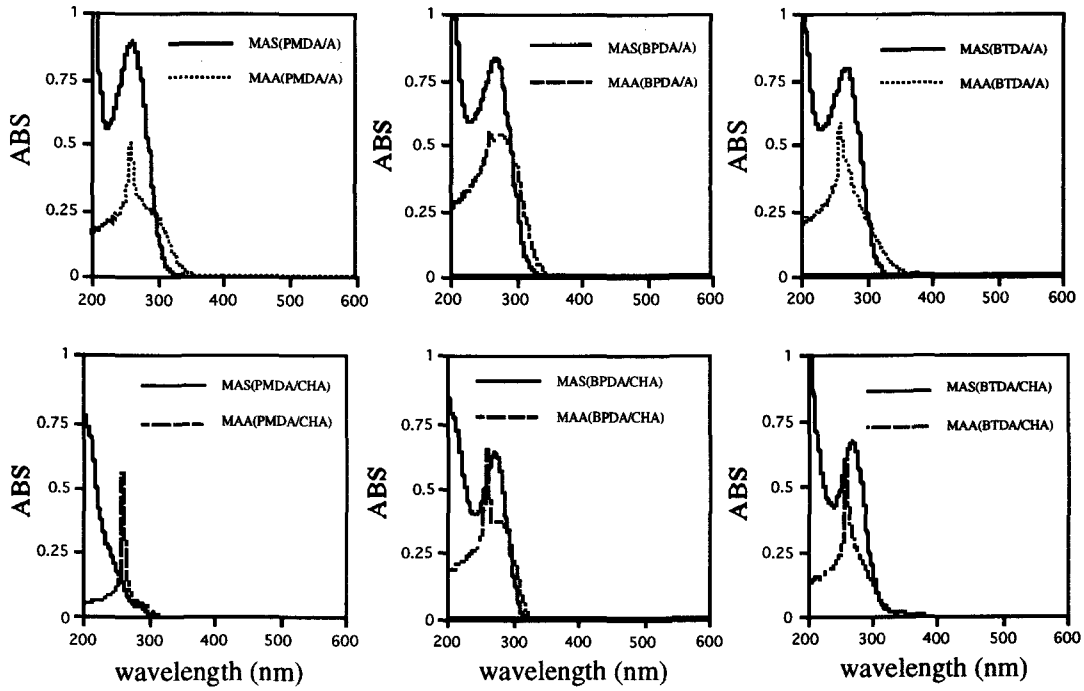

Fig.2. The UV spectra of MASs (1.60×10^{-5}M, H_2O), and MAAs (1.60×10^{-4}M, DMF, referenece, 1mm cell)

Fig.3. is the UV spectra of PASs in water and source compounds PMDA, BPDA, BTDA in CH_2Cl_2, as can be seen, the absorption of PAS(PMDA/DCHM) and PMDA are almost equal, so we can say, the differences in absorption spectra of PAS(PMDA/PDA) and MAS(PMDA/A) from those of PAS(PMDA/DCHM) and MAS(PMDA/CHA) can be related to the existence of charge transfer(CT).

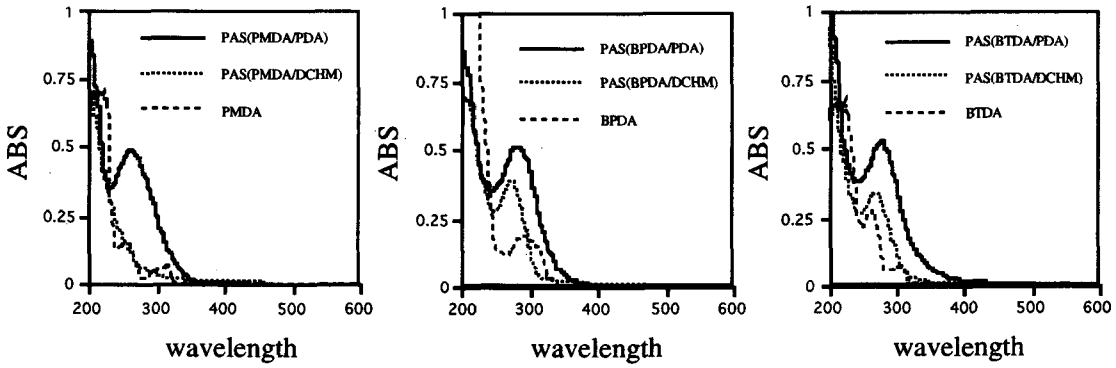

Fig.3. The UV spectra of MASs ($1.60x10^{-5}M$, H_2O) and PMDA, BPDA, BTDA($1.60x10^{-5}M$, CH_2Cl_2)

Reference

(1). K.L.Mittal, Polyimides, plenum press, NewYork, 1984

(2). H.Yoshimoto, Thesis for the degree of bachelor, 1993; T.Yamashita et al., Polymers for Microelectronics, 837(1990)